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VANADIUM METALLURGY IN THE LIGHT OF INDUSTRIAL HYGIENE AND ISSUES OF PREVENTION OF OCCUPATIONAL DISEASES AND POISONING

[Metallurgiya vanadiya v svete gigiyeny truda i voprosy profilaktiki professional'nykh zabolevanii i intoksikatsiy]

by

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Published in Gigiyena truda [Russian Journal of Industrial Hygiene] No. 9, September 1964, pp. 3-10.

Results are presented, based on investigation of industrial hygiene conditions carried out by the author at vanadium production plants undergoing modernization of outdated technological processes and assimilating newer ones. The quantitative aerosol content of the atmosphere of the working areas, as well as physical properties and chemical composition of the dispersed aerosol phase, were studied. The incidence of occupational diseases and poisoning, the presence of which may be attributed to the effects of composite aerosols and of vanadium compounds, was determined by means of systematic examination of the health of the workers. Maximum permissible concentrations of iron oxide dust containing admixtures of associated metal oxides, as well as of vanadium slag and vanadium trioxide dust, are presented. Through analysis of working conditions and the state of health of the workers, certain measures for prevention of occupational disease and poisoning are recommended by the author.

Translated for Information Services Division, EPA, from the Russian by LEO KANNER ASSOCIATES, P. O. Box 5187, Redwood City, California 94063, (415) 365-3046, February 1973.

The technical progress of modern industry is unthinkable without production of the new construction materials necessary for constructing modern machines, technological processes and the means for mechanization and automation. Many rare metals, among which vanadium occupies a prominent place, are such construction materials.

Successes in metallochemistry in recent years have made it possible to produce vanadium of high purity. The exceptionally valuable ductile, mechanical and chemical properties of this metal became known only after it had been almost completely purified of foreign matter. New vanadium compounds, its trioxide and chloride salts (VCl_3 and VCl_4) and alloys with other metals have become widespread in domestic industry, engineering and physical metallurgy. The use of carbides, chlorides and other vanadium compounds is promising.

The basic branches of industry in which vanadium and its compounds are used are high-grade steel metallurgy, production of alloys based on aluminum and titanium, the production of catalysts for the chemical industry and others.

Vanadium oxides and salts have taken on considerable occupational hygiene importance in connection with the increasing use of petroleum and fuel oils (containing considerable admixtures of this metal) as fuel for thermal electric power stations and other industrial purposes. In cleaning ashes of this fuel from boiler units, the danger arises of the toxic action of vanadium.

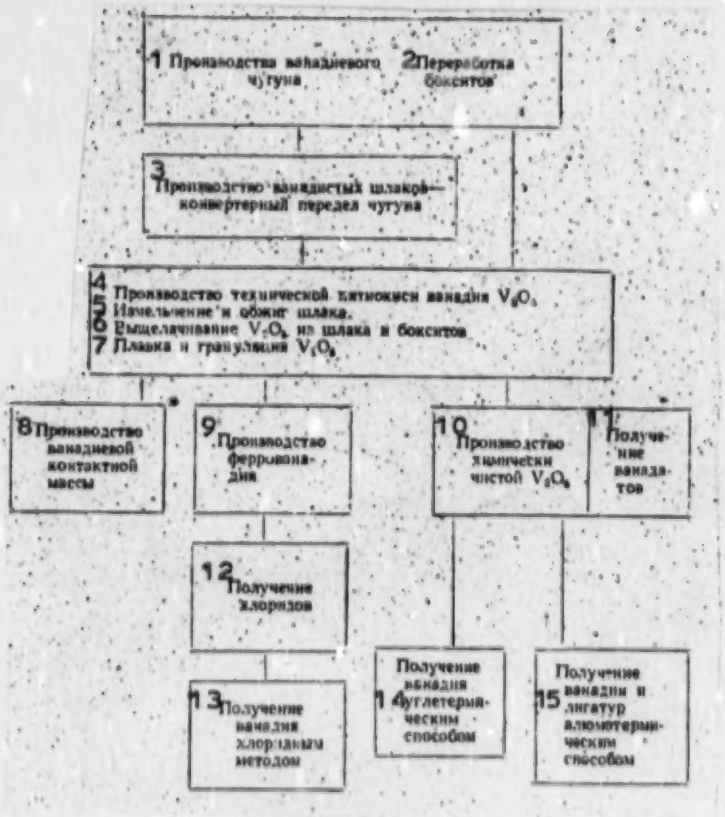
Despite the increase in production and industrial use of vanadium compounds, the assimilation of new technological processes for producing the pure metal and other pure compounds, the industrial hygiene applicable to vanadium metallurgy has not been brought to light in the literature.

Hygienic evaluations of new technological processes have not been carried out. In individual work (I.V. Roshchin), hygienic evaluation of working conditions has been given only in the extraction of technical vanadium pentoxide and ferrovanadium production. Meanwhile, in recent years, these processes have changed considerably, making the published data largely obsolete.

We took on the task of making a study of the state of health of the workers and an experimental investigation of the toxic effect of the principal vanadium compounds, on the basis of a thorough examination of working conditions, to determine the nature of occupational diseases and poisonings in vanadium metallurgy and to develop appropriate preventive measures, applicable to existing new technological processes and those being introduced into production.

Modern domestic vanadium metallurgy, a branch of ferrous metallurgy, is a complex of mutually dependent processes (see diagram), the smelting of cast iron from titanium-magnetite iron ore, the reduction of cast iron in converters for the purpose of reducing the vanadium to slag, and extraction of technical vanadium pentoxide from the slag (as well as from bauxites). Technical vanadium pentoxide serves as the raw material for production of ferrovanadium, catalyst (contact masses), chemically pure vanadium pentoxide and its salts (vanadates). Vanadium is produced from the chemically pure pentoxide by the carbon reduction and aluminum reduction methods. Vanadium tetrachloride and trichloride are produced from ferrovanadium. Metallic vanadium is produced from vanadium trichloride by reduction (the chloride method).

Diagram of production of vanadium and its compounds



1. Vanadic cast iron production
2. Bauxite treatment
3. Vanadic slag production - converter reduction of cast iron
4. Technical vanadium pentoxide V_2O_5 production
5. Slag grinding and roasting
6. V_2O_5 leaching from slag and bauxites
7. V_2O_5 fusion and granulation
8. Vanadium contact mass production
9. Ferro-vanadium production
10. Chemically pure V_2O_5 production
11. Vanadate production
12. Chloride production
13. Chloride method vanadium production
14. Carbon reduction method vanadium production
15. Aluminum reduction method vanadium and alloy production

The territorial separation of this production is of great hygienic importance, since it makes it necessary to load, pack, transport and unpack the powdered vanadium pentoxide, which has high toxicity.

The production of vanadic cast iron is not different from that of cast iron in general, from the hygienic point of view. The production of the vanadium itself begins with converter reduction of cast iron (it contains 0.5% vanadium). Converter reduction of vanadic cast iron is close to the Bessemer method of steel production in its hygienic characteristics. The atmospheric conditions are those characteristic of the Bessemer sections of steel mills.

The specific occupational danger of this process is the highly dispersed condensation aerosol, with a characteristic chemical composition of 94-95% of the dispersed phase consisting of iron oxide condensates, 2% total silicon dioxide (up to 1-1.5% being free silicon dioxide), 0.5-0.6% trivalent vanadium, trivalent chromium, manganese and titanium, and up to 1% carbon in the dust. Dust concentrations are presented in the table.

Dust and vanadium content in air in the principal vanadium metallurgy processes (data of 1200 analyses)

1 Характер процесса	2 Основной процесс	3 Основная операция, сопровождающаяся выделением аэрозоля	4 Аэрозоль	5 Наиболее частая концентрация (в мг/м³)	6 % частиц с диаметром	
					до 2 мк (7)	до 5 мк (8)
9 Подготовительные	10 Конвертерный передел чугуна	11 Продувка чугуна, заливка чугуна в конвертеры, слив готового продукта	12 Аэрозоль конденсации	17—50	76	99
	13 Измельчение ванадиевых шлаков	14 Копровая разделка шлака, дробление, помол и транспорт шлака	15 Аэрозоль измельчения ванадиевых шлаков	90—100	72	86
16 Металлохимические	17 Обжиг шлаков	18 Перевал шихты на транспортер, уборочные работы	19 Пыль шлака	10—30	74	96
			Аэрозоль ванадата натрия	0,4—0,9		
	20 Выщелачивание и осаждение V_2O_5	21 Смешивание шихты с водой	22 Аэрозоль ванадата натрия и пятиокиси ванадия	0,1—0,5	74	96
	23 Плавка и грануляция технической V_2O_5	24 Плавка, погрузочные и уборочные работы	25 Аэрозоль конденсации и измельчения V_2O_5	2—3	65	97
	26 Производство химически чистой V_2O_5	27 Просеивание, погрузка, фасовка готового продукта	28 Аэрозоль измельчения пятиокиси ванадия	2—9	70	96
	29 Получение ванадия	30 Плавка алюмотермического ванадия	31 Аэрозоль конденсации V_2O_5	0,22—0,26	76	97
		32 Приготовление шихты при получении алюмотермического ванадия	33 Аэрозоль измельчения V_2O_5	20—25	70	95
		34 Погрузка шихты при получении углетермического ванадия	35 Аэрозоль измельчения V_2O_5	19—24	83	99
	36 Производство феррованадия	37 Плавка	38 Аэрозоль конденсации V_2O_5	0,2—0,4	72	96
		39 Загрузка сырья	40 Аэрозоль измельчения V_2O_5	10—70	70	95
		41 Разделка	42 Аэрозоль измельчения феррованадия	20—30	74	93
	43 Производство катализатора	44 Помол и погрузка пятиокиси ванадия	45 Аэрозоль измельчения	3—7	60	95

[Translator's note: Commas and tabulated figures are equivalent to decimal points.]

[Key on following page]

[Key to table on preceding page]

1. Nature of process
2. Basic process
3. Principal operation accompanied by aerosol emission
4. Aerosol
5. Most frequent concentration (in mg/m^3)
6. Percent of particles with diameter of
7. Up to 2 μ
8. To 5 μ
9. Preparatory
10. Converter reduction of cast iron
11. Cast iron blow through, pouring cast iron into converters, discharge of finished product
12. Condensation aerosol
13. Grinding vanadium slags
14. Slag stamping, slag milling, grinding and transport
15. Vanadium slag grinding aerosol
16. Metallochemical
17. Slag roasting
18. Batch transfer to transporter, clean up work
19. Slag dust sodium vanadate aerosol
20. V_2O_5 leaching and precipitation
21. Mixing batches with water
22. Sodium vanadate and vanadium pentoxide aerosol
23. Technical V_2O_5 fusion and granulation
24. Fusion, loading and cleanup work
25. V_2O_5 grinding and condensation aerosol
26. Chemically pure V_2O_5 production
27. Screening, loading, packing finished product
28. Vanadium pentoxide grinding aerosol
29. Vanadium production
30. Aluminum reduction vanadium fusion
31. V_2O_5 condensation aerosol
32. Batch preparation during aluminum reduction vanadium production
33. V_2O_5 grinding aerosol
34. Batch loading during carbon reduction vanadium production
35. V_2O_5 grinding aerosol
36. Ferrovanadium production
37. Fusion
38. V_2O_5 condensation aerosol
39. Raw material charging
40. V_2O_5 grinding aerosol
41. Dressing
42. Ferrovanadium grinding aerosol
43. Catalyst production
44. Vanadium pentoxide grinding and loading
45. Grinding aerosol

Aerosol formation and entry into the working area takes place continuously. Workers are constantly in the zone of the dust concentrations specified. Removal of the aerosol directly from the converter throat outside the working premises is made difficult by the fact that, for technical reasons, blowing through the cast iron with compressed air takes place with the converter in changing positions, in the horizontal, inclined and vertical positions. In this case, the aerosol is removed by exhaust ventilation in the form of a natural draft shaft only in blowthrough in the vertical position. In the remaining converter positions, the aerosol goes into the room.

Stamp-mill preparation of the large-sized slag ingots, crushing in hammer mills, grinding and roasting in horizontal rotary furnaces at 800° precedes vanadium pentoxide extraction from the converter slags. All of these processes are accompanied by severe dust formation.*

The principal causes of the great dustiness of the air are the stamp-mill slag preparation, which does not permit the sources of dust formation to be localized and closed off, and, as well, does not provide for a continuous method of slag dressing; frequent transfers of the ground slag; open loading; leaks in the mills, ground raw material transporters and magnetic separators; and the dry cleanup of the premises.

Vanadium oxide and salt aerosols are the principal occupational hazards of all the metallochemical processes. The most widespread poison among them is vanadium pentoxide. In loading, moving, packing, grinding, batch preparation, granulation (production of technical and chemically pure vanadium pentoxide, production of metallic vanadium, production of vanadium catalyst and other

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*A hygienic evaluation of the slag dust and the picture of the pneumoconiosis caused by it was given by us in the Journal, Gigiyena i sanitariya, 1963, No. 12.

things), it forms a grinding aerosol. In the processes of fusing it, and alloy and metallic vanadium smelting, a condensation aerosol is formed, which is distinguished by a higher degree of toxicity.

As is seen from the table, the condensation aerosol content normally is low, due to covering of the smelting equipment (vanadium smelting) and devices for local exhaust ventilation of smelting furnaces and electric furnaces. On the other hand, the grinding aerosol concentrations are high and they fluctuate sharply during the entire working day, that is, they are reduced in the intervals between operations and are increased at times when dusty operations are carried out (pentoxide loading during ferrovanadium smelting, catalyst and chemically pure pentoxide production, during vanadium smelting, and at other times).

The vanadium pentoxide dust concentrations found in the air are capable of showing an acute toxic action, but intoxication symptoms usually are not observed, since the workers use "Lobe" respirators.

The vanadium compound dust concentrations are particularly significant in the new processes of reduction of its pentoxide and metallic vanadium production. As a consequence of the separation mentioned of individual works from one another, in the production of chemically pure vanadium pentoxide, a single process, with covered operations for batch preparation, making the processes of reduction of the pentoxide to vanadium trioxide air tight, mixing of the dusty materials and loading them into the smelting equipment, cannot be established.

Vanadium trioxide, because of its hygienic importance, occupies an important place after vanadium pentoxide. Its dust is one of the leading hazards in carbon reduction metal production. Besides, vanadium trioxide, as was indicated above, is a component part of the vanadium slag and fuel oil ash dusts.

As our research has shown, vanadium trioxide is less toxic than the pentoxide. Nevertheless, during batch preparation, in the absence of special means of protection of the workers, the vanadium trioxide concentration can have

subacute and chronic toxic effects. Contamination of the air with vanadium trioxide takes place because of the open discharge of batches from the mixers after they are mixed and the absence of local exhaust ventilation during these operations.

Certain characteristics of the course of occupational illnesses and intoxication were established by means of a detailed, systematic examination of the state of health of 300 workers.*

Among 41 converter operators examined, who were subjected to the action of the aerosol indicated, pneumoconiosis was revealed in 10 (in 4, stage II, and in the remainder, stage I). The ages of those ill were from 34 to 51 years. They had from 12 to 18 years experience in their work. Pneumoconiosis of the converter operators was manifested by distinct radiological changes of a nodular character. Multiple, fine-node shadows were distributed on the background of diffuse deformations of the bronchial-vascular picture. In the stage I illness the workers complained only of coughing. Objective examination of them disclosed no significant deviations from normal. In persons with the stage II illness, shortness of breath during physical work, hard breathing and multiple dry rattles in the lungs were noted.

In view of the X-ray contrast of the dust (iron oxides), it should be assumed that productive changes in the lungs are not so pronounced as represented on the X-ray photos. Nevertheless, this process is a pathological condition, especially during the stage II illness. Converter operator pneumoconiosis is similar in its X-ray manifestations to electric welder pneumoconiosis. The data obtained indicates a definite danger of pneumoconiosis from the aerosols

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*Candidate in medical sciences P. S. Kublanova, candidate in medical sciences M. D. Bagnova, G. V. Bulychev, A. A. Komarova, V. B. Usman, V. C. Ruzhentsova, and K. A. Dmitriyeva; Plant surgeon, L. M. Markova; candidate in biological sciences, N. N. Pushkina; candidates in biological sciences L. V. Zhidkova, L. A. Lutsenko, A. Ya. Dushen'kina, A. M. Tambovtseva, and A. V. Il'nitskaya participated in the examinations. Candidate in medical sciences Ye. P. Krapukhina was consulted on the examination materials.

formed during the converter reduction of cast iron. The campaign against this dust takes on greater and greater importance, in connection with the spreading use of the converter method of steel production in metallurgy.

Slag pneumonoconiosis, on the other hand, is distinguished by an unfavorable course, caused by the combined action of the vanadium trioxide, trivalent chromium and free silicon dioxide in the dust.*

We also studied occupational diseases of workers chronically subjected to the action of the vanadium pentoxide aerosol. For this, 116 workers were examined dynamically and the remainder were examined once. In this case, diseases of the upper respiratory tract, (rhinitis, with erosion and scars of the mucuous membrane of the nose, pharyngitis) were established in 71% of those examined, and these diseases arise with work experience of from 1 to 5 years. Also, chronic bronchitis usually was sharply expressed, and it was found in 40% of those examined. It arises most frequently with 10 years work experience. Diffuse pneumosclerosis was established in 12.6% of those examined. This disease is characterized by shortness of breath when working, rapid fatigue, band box sound and hard, somewhat weakened breathing and accentuation of the second sound in the pulmonary artery. Upon X-ray examination of the patients, an increase in reticulation of the pulmonary picture, dilation and tubular heaviness of the lung roots and emphysema were found. The disease arises in persons who have worked from 10 to 20 years and longer under the influence of vanadium pentoxide at concentrations of from 1 to 5 mg/m^3 on the average.

Diseases of the respiratory organs are accompanied by weakly expressed anemia, dysproteinemia, (decrease in albumins and increase in α- and γ-globulin fractions), a tendency towards hypocholesterinemia, as well as an increased

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*Gigiyena i sanitariya, 1963, No. 12.

frequency (in comparison with the control group) in nonspecific functional disorders of the nervous system (asthenic-vegetative syndrome, suppression of the corneal reflexes, increase in neuromuscular excitability, and vegetative-vascular reactions). Changes in the cardio-vascular system are similar to those which are observed in slag pneumoconiosis. Our data let it be indicated that chronic vanadium compound intoxication is present, the possibility of which is not granted by all foreign authors.

There is a considerable danger of acute poisoning in work connected with the production of chemically pure vanadium pentoxide, forged vanadium and vanadium chlorides. Poisoning can be caused by even a brief action by vanadium pentoxide and salts in concentrations greater than 10 mg/m^3. In this case light cases of poisoning are observed more often. More serious and acute poisonings are encountered in cleaning the ash accumulations formed in burning of heavy fuel oil from electric power station boilers.*

It is very important to accomplish the necessary preventive measures, in view of the expansion of vanadium metallurgy and the establishment of new production processes. In this regard, it would be of special hygienic importance to combine the separate manufacture of technical and chemically pure vanadium pentoxide, the production of vanadium and its alloys, which up to now have been separated, into a continuous process. This would allow the most unfavorable operations to be completely excluded: technical vanadium pentoxide grinding, packing, loading, and unpacking of the technical and pure vanadium pentoxide. The combination of these manufacturing processes into a continuous system would make it possible to use vacuum transport for moving vanadium pentoxide, and covering and local exhaust ventilation of dust formation sources.

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*Gigiyena truda i professional'nyye zabolevaniye, 1962, No. 5.

The provision of continuous production of technical vanadium pentoxide and ferrovanadium in a newly constructed plant, in which the vanadium pentoxide, after its fusion, eliminating the granulation stage, would be filled into the electric furnace in liquid form for ferrovanadium smelting, is highly effective from the hygienic point of view. This excludes the possibility of formation of disintegration aerosols, the concentrations of which are so significant, during granulation, loading and charging of the granulated product into the electric furnace.

It is important to replace dry grinding by wet in production of catalyst and pure vanadium pentoxide. In this way, the vanadium pentoxide dust concentration is reduced from 5 - 10 mg/m^3 to permissible limits.

Aluminum reduction vanadium smelting must be carried out in completely closed boxes, with complete removal of the aerosol at the moment of its violent formation by use of local exhaust ventilation from under the box cover.

Small manual operations in experimental and physical metallurgy work, as well as in industrial production of vanadium trioxide, metallic vanadium and pure vanadium pentoxide (weighing oxides and salts, packaging them, and mixing batch materials) should be accomplished only in exhaust hoods with effective local exhaust ventilation. In this case, the concentrations of pentoxides, trioxides and ammonium vanadate in the breathing area must not exceed the permissible limits which we have recommended.

The necessary reduction in slag dust in the air is achieved by the introduction of vacuum transport for transferring the ground slag from the mills to the roasting furnaces, and from the roasting furnaces to vanadium pentoxide leaching. However, the dustiness of the air still remains high in the primary grinding sections. In accordance with our recommendations, to reduce it, the slag stamp-mill must be eliminated and replaced by crushing in hammer mills. For this purpose production of slag in small ingots must be laid on in the converter section.

At the present time, the State Scientific Research and Planning Institute of the Metallurgical Industry is developing a project for reconstruction of primary slag grinding, for reduction of dustiness of the air. Provision of continuous primary slag grinding permits the hammer mill, magnetic separator and other sources of dust emission to be covered, and the use of local exhaust ventilation from dusty equipment, as well. At points of possible dust emission through leaks in mills and magnetic separators, a good effect is achieved by introduction of dry foam to foci of dust formation. This reduces the dustiness of the air to permissible values. The foam is produced in a simple device, by means of blowing air through a mixture of joiner's glue (9%), a detergent mixture of sulfonaphthenic acids (Russian equivalent of Twitchell reagent) in kerosene (60%), water (20.7%) and crude spirits (10.3%).

Wet cleaning of the premises, carried out systematically, is of great importance for reducing the dust content in the air.

In the event of the presence of vanadium in concentrations exceeding those permitted in the air of working areas, it is recommended that the "Lobe" respirators, which satisfactorily protect the respiratory organs from dust, be used in individual operations.

The high technical level of new vanadium metallurgy plants makes it possible to organize remote control of a number of processes and it eliminates the continual presence of workers in areas of possible dust formation, especially in slag roasting, fusion and grinding of technical vanadium pentoxide, and in roasting of ammonium vanadate.

Reduction of dust concentration in converter sections, particularly in the converter reduction of vanadic cast iron, is a difficult, still unsolved problem. Support must be given to a special search for effective methods of removing large masses of aerosols directly from the converter throat away from the working areas, with subsequent dust trapping.

For early detection of occupational diseases, medical examination of converter operators and mixer operators must be carried out once every two years by a therapist and a radiologist. It is recommended that workers subject to the action of slag dust be examined annually by an otolaryngologist and every two years by a radiologist. It is advisable for workers subject to the action of vanadium oxide and salt dust to be examined annually by a committee composed of an otolaryngologist, a therapist and a hematologist. X-ray examinations may be carried out once every two years.

On the basis of study of the state of health of the workers, in close connection with industrial-hygienic and experimental-toxicological research, in addition, we have established permissible concentration limits for aerosols

vanadium metallurgy plants: iron oxide aerosols with admixtures of small quantities of the oxides of silicon, vanadium, chromium, manganese and titanium (converter reduction of cast iron) 6 mg/m^3, vanadium-containing slag dust, 4 mg/m^3, and vanadium trioxide dust, 1 mg/m^3.

Accomplishment of the set of technical, sanitary-hygienic and medical measures permits prevention of occupational diseases and poisonings in the industrial production and use of vanadium.

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